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Organometallics, **1994**, 13 (10), 3770-3772• DOI: 10.1021/om00022a008 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street
N.W., Washington, DC 20036

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Reversible Carbene−Carbyne Interconversion on a Trinuclear Cluster

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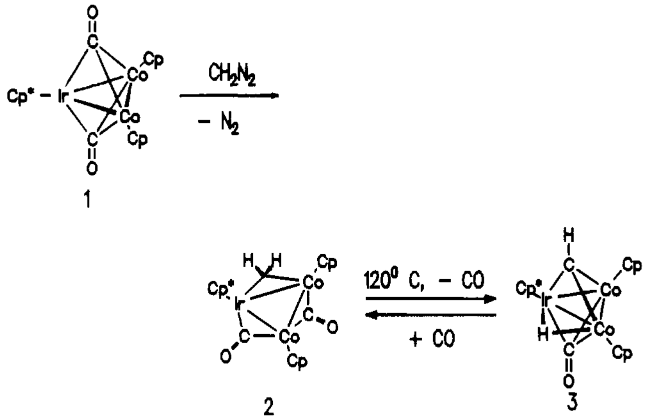
Received June 20, 1994®

Summary: Refluxing the carbene complex $(\mathrm{Cp^*Ir})(\mathrm{CpCo})_2(\mu\text{-}\mathrm{CO})_2(\mu\text{-}\mathrm{CH}_2)$ ***(2)*** *in toluene yields the carbyne hydride complex* $(\mathrm{Cp^*Ir})(\mathrm{CpCo})_2(\mu\text{-}\mathrm{CO})(\mu_3\text{-}\mathrm{CH})(\mu\text{-}\mathrm{H})$ ***(3)****. Variable-temperature NMR studies on* ***3*** *reveal two fluxional processes with different activation energies: slow exchange of the hydride ligand with the methylidyne hydrogen and rapid migration of the hydride ligand between different edges of the metal triangle. Exposure of* ***3*** *to CO at room temperature re-forms* ***2*** *quantitatively.*

Carbene and carbyne ligands on metal surfaces are believed to be intermediates in heterogeneous alkane activation and Fischer−Tropsch chemistry.[1] Molecular cluster complexes containing these ligands have been used to model some of the hypothesized steps involved in these heterogeneous processes.[2] To date, most efforts in this area have focused on carbonyl-based cluster systems.[3,4] Much less is known about Cp- and Cp*-based cluster systems, and only a few reports about such systems containing carbene or carbyne ligands have appeared.[5,6]

Recent efforts in our group have been focused on the reactivity of the Cp-based unsaturated, 46 e$^-$ trinuclear clusters of the form $\mathrm{Cp^*M(CpCo)_2(CO)_2}$ (M = Co, Rh, Ir).[7] These cluster complexes are unsaturated and readily add donor ligands such as carbon monoxide and alkynes.[8] The complex $\mathrm{Cp^*Ir(CpCo)_2(CO)_2}$ (**1**) also forms the carbene adduct $\mathrm{Cp^*Ir(CpCo)_2}(\mu\text{-}\mathrm{CO})_2(\mu\text{-}\mathrm{CH}_2)$ (**2**), upon reaction with diazomethane, as described by Herrmann et al.[6] In this communication we report that when **2** is heated in toluene, CO is lost and the carbyne hydride complex $\mathrm{Cp^*Ir(CpCo)_2}(\mu\text{-H})(\mu_3\text{-CH})(\mu\text{-CO})$ (**3**) is formed.



When a toluene solution of **2** is heated to reflux for 2 h, carbon monoxide is lost and the carbyne hydride complex **3** may be isolated in 74% yield after chromatography (ether/hexane). At 190 K the ^{1}H NMR spectrum of **3** shows two distinct resonances for the protons of the Cp ligands and one signal for the Cp* protons. The hydride and methylidyne proton signals occur at −25.7 and 14.5 ppm, respectively.[9] These chemical shift values are consistent with a structure which does not contain agostic interactions involving these ligands.[4c,10] The ^{13}C chemical shift of the methylidyne carbon (265 ppm) and temperature-independent C−H coupling constant for this ligand ($^1J_{\mathrm{CH}}$ = 162 Hz) also argue against agostic interactions in the complex at low temperature.[4c,10] The low stretching frequency for the carbonyl ligand (1690 cm^{-1}) is consistent with a μ_3 coordination geometry for this ligand and, if it is assumed that the methylidyne ligand is also triply bridging, then the hydride ligand must occupy a briding coordination geometry across one Ir−Co bond at low temperature.

When the temperature is increased, coalescence of the two Cp signals for **3** is observed (T_c = 194 K for ^{1}H, T_c = 205 K for ^{13}C) and a single, sharp signal which accounts for the protons of both Cp rings results at room temperature. Complete line shape analysis[11] of the proton NMR data yields a rate constant of 111 s^{-1} at

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® Abstract published in *Advance ACS Abstracts,* September 1, 1994.

[1] Sheppard, N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 589. Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 12.

[2] Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91−135. Muetterties, E. L. *Pure Appl. Chem.* **1982**, *54*, 83−96.

[3] (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225−5226. (b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726−7727. (c) Shapley, J. R.; Cree-Uchiyama, M. E.; St. George, G. M. *J. Am. Chem. Soc.* **1983**, *105*, 140−142. (d) Holmgren, J. S.; Shapley, J. R. *Organometallics* **1984**, *3*, 1322−1323. (e) Holmgren, J. S.; Shapley, J. R. *Organometallics* **1985**, *4*, 793−794. (f) Yeh, W. Y.; Wilson, S. R.; Shapley, J. R. *J. Organomet. Chem.* **1989**, *371*, 257−265.

[4] (a) Wong, K. S.; Fehlner, T. P. *J. Am. Chem. Soc.* **1981**, *103*, 966−967. (b) Vites, J. C.; Jacobson, G.; Dutta, T. K.; Fehlner, T. P. *J. Am. Chem. Soc.* **1985**, *107*, 5563−5565. (c) Dutta, T. K.; Vites, J. C.; Jacobsen, G. B.; Fehlner, T. P. *Organometallics* **1987**, *6*, 842−847. (d) Barreto, R. D.; Fehlner, T. P. *J. Am. Chem. Soc.* **1988**, *110*, 4471−4472. (e) Fehlner, T. P. *Polyhedron* **1990**, *15/16*, 1955−1963.

[5] (a) Vollhard, K. P.; Fritch, J. R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 559−561. (b) Wadepohl, H.; Pritzkow, H. *J. Organomet. Chem.* **1993**, *450*, 9−19. (c) Kersten, J. L.; Rheingold, A. L.; Theopold, K. H.; Casey, C. P.; Widenhoefer, R. A.; Hop, C. E. *Angew. Chem.* **1992**, *104*, 1346; *Angew. Chem., Int. Ed. Engl.* **1992**, *32*, 1341. (d) Casey, C. P.; Widenhoefer, R. A.; Hallenbeck, S. L. *Organometallics* **1993**, *12*, 3788−3789.

[6] Herrmann, W. A.; Barnes, C. E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1985**, *4*, 172−180.

[7] Barnes, C. E.; Dial, M. R. *Organometallics* **1988**, *7*, 782−784. Barnes, C. E.; Dial, M. R.; Orvis, J. A.; Staley, D. L.; Rheingold, A. L. *Organometallics* **1990**, *9*, 1021−1035.

[8] Barnes, C. E.; Orvis, J. A.; Finnis, G. M. *Organometallics* **1990**, *9*, 1695−1697.

[9] ^{1}H NMR (400 MHz, toluene-d_8, T = 190 K): δ 14.85 (1H), 4.84 (5H), 4.72 (5H), 1.73 (15H), −25.68 (1H). ^{13}C NMR: δ 265 (d, J_{CH} = 162 Hz), 241.3 (s), 102.7 (s), 89.5 (d), 86.7 (d), 15.3 (q). IR: ν_{CO} 1690 cm^{-1}. MS (EI): m/e 618 (M$^+$ based on ^{193}Ir). Anal. Calcd: C, 42.79; H, 4.22. Found: C, 42.98; H, 4.50.

[10] Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1−124.

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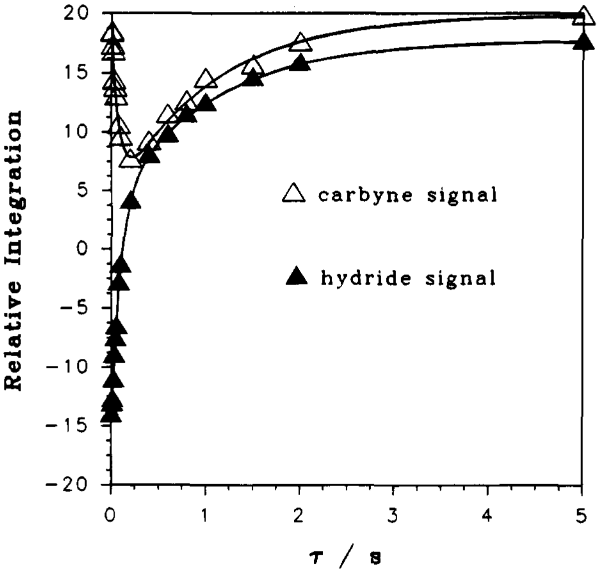


Figure 1. Experimental (triangles) and calculated (lines) intensities[13] for the selective inversion transfer experiment performed on **3** at 275 K with the hydride signal inverted. Shown are both the μ_3-CH and μ-H signals at different τ values.

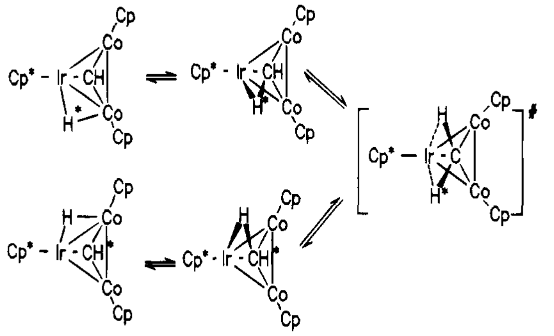
194 K. Using rate constants from temperatures between 180 and 270 K, a free energy of activation $\Delta G^{\ddagger}$ at 300 K of 45(2) kJ mol^{-1} was obtained for this process.

In addition to the changes described above, the carbyne and hydride resonances are slightly broadened at room temperature when compared with the low-temperature spectrum. A NOESY spectrum for **3** (τ = 30 ms) shows a strong, positive cross peak between these two signals consistent with chemical exchange of these two hydrogen atoms.

A slow exchange process which does not cause coalescence of the resonances involved may be monitored by magnetization transfer experiments.[12] One variant of this experiment involves selectively applying a 180° pulse to one of the exchanging nuclei and monitoring the transfer of the effect of this pulse to the other nuclei involved in the exchange process. Figure 1 shows the results of such an inversion transfer experiment where the hydride resonance in **3** has been inverted. Analytical fits to the data for both the carbyne and the hydride resonances give rate constants for the exchange process.[12c,13] At 275 K a rate constant of about 5.0(5) s^{-1} is found. Repetition of the experiment at different temperatures (250–300 K) gives an activation energy for the exchange process $\Delta G^{\ddagger}$(300 K) = 63(2) kJ mol^{-1}.

The different activation energies obtained from line-shape and inversion transfer experiments lead to the conclusion that two different fluxional processes take place in **3**.[14] For the exchange of the methylidyne proton and hydride ligands we propose a mechanism which involves agostic (C–H–M) interactions, as illustrated in Scheme 1. The sequence of steps shown here is similar to mechanisms proposed for the carbonyl-based cluster $M_3(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CH)$ (M = Ru, Os).[15] The initial step of this process involves the hydride ligand moving from a metal–metal edge to an "agostic" geometry on a metal–$C_{\text{methylidyne}}$ edge. Qualitative analysis of the energetics of agostic interactions in homo- and heteronuclear clusters of iron, ruthenium, and osmium[16] suggest that C–H–M bridging hydrogens will prefer the metal with the lower electronegativity, which, in the case of **3**, is the Ir–C edge. A transition state in which the M–H interaction is released simultaneously with the methylidyne hydrogen moving toward an "agostic" position on the opposite C–H–M edge then exchanges the identities of these protons. The final step is simply the reverse of the initiating step, with the former terminal carbyne hydrogen now ending up on the opposite Ir–Co edge.

Scheme 1



Although the mechanism described above equilibrates the two CpCo vertices in **3**, our kinetic analyses indicate that a second, lower energy process must also be available to accomplish this task without exchanging the hydride and methylidyne hydrogen identities. Migration of hydride ligands in several tri- and tetranuclear cluster systems has been observed with similar activation energies[5b,17] and may simply involve movement of the hydride ligand from the ground-state bridging geometry to a terminal coordination mode and finally back to a bridging mode on a different metal edge in the complex. However, in some of the systems mentioned above, alkylidyne ligands are also present and may be involved in these processes. A possible mechanism which would include the carbyne ligand in hydride migration involves reversible movement of the bridging hydride ligand to an agostic position on the Ir–C edge in **3** without moving the carbyne hydrogen. Since the terminal carbon–hydrogen bond is not broken in this case, a lower activation barrier compared with the carbyne–hydride exchange can be expected for this process. Our data do not allow us to distinguish between different mechanisms for the hydride edge

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[11] Binch, G.; Kessler, H. *Angew. Chem.* **1980**, *92*, 445–463; *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411–428.

[12] (a) Forsen, S.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *39*, 2892–2901. (b) Alger, J. R.; Prestegard, J. H. *J. Magn. Reson.* **1977**, *27*, 137–141. (c) Mariappan, S. V.; Rabenstein, D. L. *J. Magn. Reson.* **1992**, *100*, 183–188.

[13] Fit parameters were the rate constant for the exchange *k*, the relaxation times T_1(CH) and $T_1(\mu\text{-}H)$, and the initial magnetization of the observed resonance. The relaxation times for the carbyne and the hydride protons were found to be completely averaged by the exchange at 300 K, resulting in only one observed relaxation time of 1.6 s. Therefore, only an average relaxation rate was used for the fits above 270 K. At lower temperatures, two distinct relaxation times were measured and used as starting values in the model.

[14] That two processes are present becomes even more obvious when one compares the rate constants derived from data in the different temperature ranges. For the process equilibrating the CpCo edges, k = 111 s^{-1} at 194 K, whereas hydrogen atom exchange between carbyne and hydride sites has a lower rate constant of 5 s^{-1} at 275 K.

[15] VanderVelde, D. G.; Holmgren, J. S.; Shapley, J. R. *Inorg. Chem.* **1987**, *26*, 3077–3078.

[16] Fehlner, T. P. *Polyhedron* **1990**, *9*, 1955–1963.

[17] Van Horn, D. E.; Vollhard, K. P. C. *J. Chem. Soc., Chem. Commun.* **1982**, 203–204.

exchange. However, a mechanism involving agostic hydrogens could explain why $Cp^*Rh(Cp^*M)_2(CO)_2(\mu\text{-}H)_2$ (M = Co, Ir)[18] and $Os_3Pt(\mu\text{-}H)_2(CO)_{10}P(C_6H_{11})_3$,[19] which do not have carbyne ligands, exhibit much higher activation energies for hydride migration around their metal skeletons.

The facile exchange of hydrogen atoms between the methylidyne and hydride sites suggests that it may be possible to transform the carbyne hydride complex **3** into a carbene complex if a ligand was present to supply the two valence electrons which are lost when the hydride migrates to the methylidyne carbon. Consistent with this prediction, we find that **3** quantitatively re-forms the carbene complex **2** when exposed to CO at room temperature.[20] On the other hand, the isoelectronic osmium carbonyl cluster $Os_3(CO)_{10}(\mu\text{-}CH)(\mu\text{-}H)$ (**4**) does not exhibit hydrogen atom exchange between the carbyne and hydride sites and also does not add carbon monoxide. Instead, nucleophiles attack directly at the carbyne carbon.[3c] The trihydride clusters $M_3(CO)_9(\mu_3\text{-}CH)(\mu\text{-}H)_3$ (M = Ru, Os)[15] do exhibit hydrogen atom transfer between the methylidyne and hydride ligands, but with higher values of $\Delta G^{\ddagger}$ (86 kJ mol^{-1} for M = Ru and 100 kJ mol^{-1} for M = Os). However, none of these systems are observed to add CO, even at higher temperatures.[15]

To our knowledge this is the first example of a Cp-based cluster complex for which hydrogen exchange between carbyne and hydride sites is observed and one of only a few systems exhibiting reversible carbene to carbyne hydride interconversion.[4c] The above observations indicate that the lower the barrier of activation for the carbyne hydride exchange, the more reactive the cluster will be toward addition of nucleophiles. The reason for this increased reactivity is the fact that the high mobility of the hydrogens between the hydride and the carbyne sites enables the cluster to easily "switch" between a carbyne and a carbene species, the latter opening up a coordination site to allow the addition of a ligand. Current investigations are directed at investigating the reactivity of **3** toward ligands other than CO.

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(18) Bray, A. C.; Green, M.; Hankey, D. R.; Howard, J. A.; Johnson, H.; Stone, F. G. A. *J. Organomet. Chem.* **1985**, *285*, C12–C16.

(19) Ewing, P.; Farrugia, L. J.; Rycroft, D. S. *Organometallics* **1988**, *7*, 859–870.

(20) Quantitative conversion of **3** to **2** is observed within 2 h at 270 K (toluene-d_8). Longer exposure to CO leads to cluster fragmentation.